Local lattice potentials and steady-state vacancies in ionic crystals

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Basing on peculiarities of local potentials, the two principal trends in vacancy formation are revealed. The proximity to the threshold of local ionic stability due to a giant potential contribution of electronic delocalization accounts for thermal anion vacancies typical of intrinsic semiconductors of AB type. On the other hand, the tendency towards equalizing the potential field results in a high concentration of structural cation vacancies observed in Ni$_3$Sb and relative compounds.

Bulk electrostatic potential field plays a fundamental role in crystals [1], for it specifies both the electronegativity [1, 2, 3] and charge transfer [4, 5, 6, 7] and eventually contributes to the cohesive energy there [8, 9, 10]. Described by lattice series [8, 9, 11, 12], bulk potentials can nevertheless be defined as unique quantities subjected to invariant periodic boundary conditions [13, 14]. The particular event of point charge lattices is of special interest [15, 16, 17, 18, 19, 20, 21, 22, 23, 24, 25, 26] because it is relevant to spherically symmetric ions of which external potential effect amounts to that of point charges [27]. However, the symmetry of ionic potentials evident in this case [1, 28, 29, 30, 31, 32, 33, 34] cannot explain the known fact that the steady-state concentrations of vacancies of various ionic species differ even in the simplest case of diatomic crystals [35]. The nature of abnormal concentrations of cation vacancies in Ni$_3$Sb and relative compounds [36, 37, 38] is one more intriguing problem.

In the present paper we discuss in detail that the effect of prevailing anion vacancies inherent in GaAs [39, 40, 41, 42] as well as in structurally relative nitrides [43, 44, 45, 46] can be understood if the potential contribution of electronic delocalization [13, 34, 47] is taken into account. But it turns out that another treatment based on lattice potentials is appropriate to explain cation vacancies in question.

To discuss local properties in ionic crystals, we consider a crystal composed of j ionic species per unit cell, with basis vectors $\mathbf{b}_j$ and with total charges q_j described by charge distributions $\rho_j(\mathbf{r})$ spherically symmetric for simplicity. According to [13, 14, 34], the bulk electrostatic potential $U_\mathrm{b}(\mathbf{r})$ at a point $\mathbf{r}$ can be written as follows:

$$U_\mathrm{b}(\mathbf{r}) = U_\mathrm{Cd}(\mathbf{r}) + \Phi_\mathrm{top}, \qquad (1)$$

where

$$U_\mathrm{Cd}(\mathbf{r}) = {\sum_i}' \sum_j \int_{V_j} \frac{\rho_j(\mathbf{r}')\, d\mathbf{r}'}{|\mathbf{r}' + \mathbf{R}_i + \mathbf{b}_j - \mathbf{r}|}, \qquad (2)$$

$$\Phi_\mathrm{top} = \frac{2\pi}{3v} \sum_j \int_{V_j} |\mathbf{r} + \mathbf{b}_j|^2 \rho_j(\mathbf{r})\, d\mathbf{r}, \qquad (3)$$

the sum over i runs over the Bravais lattice specified by $\mathbf{R}_i$, the prime on the summation sign implies missing the

singularities of the summand, V_j is the volume of integration appropriate to $\rho_j(\mathbf{r})$, v is the volume of the unit cell. It is important that the absolute convergence of interest can always be achieved for (2) by introducing fictitious point charges, which in turn can be included into the set over j [13, 14]. Note that if the distributions $\rho_j(\mathbf{r})$ are non-overlapping, then (2) describes the potential in the point-charge lattice, but (3) can be represented as

$$\Phi_\mathrm{top} = \frac{2\pi}{3v} \sum_j |\mathbf{b}_j|^2 q_j + \Phi_\mathrm{top}^\mathrm{deloc}, \qquad (4)$$

$$\Phi_\mathrm{top}^\mathrm{deloc} = \frac{2\pi}{3v} \sum_j \int_{V_j} |\mathbf{r}|^2 \rho_j(\mathbf{r})\, d\mathbf{r}, \qquad (5)$$

where the first term on the right-hand side of (4) modifies the result of (2) so as to retrieve the potential symmetry in a point-charge lattice, but $\Phi_\mathrm{top}^\mathrm{deloc}$ determines the potential contribution of electronic delocalization in ions, providing that this potential shift is intrinsically negative and additive with respect to all ions in question [13, 34].

Based on (1), the bulk Coulomb energy takes the form

$$\mathcal{E} = \frac{1}{2} \sum_j q_j\, U_j^\mathrm{eff}, \qquad (6)$$

where the contribution of fictitious charges mentioned above vanishes by definition, so that j runs over all the actual ions in the unit cell [13, 34],

$$U_j^\mathrm{eff} = \frac{1}{q_j} \int_{V_j} \rho_j(\mathbf{r})\, U_\mathrm{b}(\mathbf{r} + \mathbf{b}_j)\, d\mathbf{r}. \qquad (7)$$

In the foregoing case of point-like charges, U_j^eff are reduced to the corresponding point-charge-lattice ionic potentials U_j^0 [13, 34], but shifted by $\Phi_\mathrm{top}^\mathrm{deloc}$.

It is significant that every ion should be bound energetically in the lattice. This claim implies that

$$q_j\, U_j^\mathrm{eff} < 0, \qquad (8)$$

despite the fact that according to (6) and the overall neutrality of the unit cell, the entire value of $\mathcal{E}_\mathrm{b}$ is indifferent to any uniform shift of the potential values. Hence, negative ions are to stay in positive potential fields, so that

the admissible negative value of $\Phi_{\mathrm{top}}^{\mathrm{deloc}}$ appears to be restricted for every actual ionic structure and the lattice instability should be expected otherwise.

Note that Φ_{top}^{deloc} does not change relative values on the bulk potential map, but describes the binding energies relative to free ions, with including their own stability [48, 49, 50]. Therefore, it can be essential in the problem of steady-state vacancies forming at high temperatures. To estimate this effect, let a vacancy be generated by the simple exclusion of an ion from its regular position without any relaxation of the surroundings [18, 35, 51, 52, 53]. The total concentration of vacancies is assumed to be small enough, so that their influence on the bulk potentials [6, 54, 55] can be ignored at least while we are interested in thermal vacancies. The energy loss appropriate to a vacancy of the jth species is then as follows:

$$E_j^{\mathrm{vac}} = -q_j\,U_j^{\mathrm{eff}}. \tag{9}$$

Based on (9), the steady-state concentrations n_j of vacant states can be defined by the Boltzmann relation as

$$n_j = w_j \exp\left(-\frac{E_j^{\mathrm{vac}}}{k_{\mathrm{B}}T}\right), \tag{10}$$

where w_j is the number of energetically equivalent ions of the jth species in the unit cell, k_{B} is the Boltzmann constant, T is the temperature. The inequality $E_j^{\mathrm{vac}} > 0$ follows from (8)–(10) as a necessary condition for $n_j \ll 1$.

To make the further discussion complete, we start from the simplest case of AB compounds described by point-charge lattices [47]. Then there are only two charge species with $q_+ = -q_- = \kappa$, $w_\pm = 1$, and

$$E_\pm^{\mathrm{vac}} = \kappa\big(U_-^0 \mp \Phi_{\mathrm{top}}^{\mathrm{deloc}}\big), \tag{11}$$

where U_-^0 is the point-charge-lattice potential on q_-. According to (10) and (11), for the ratio n_-/n_+ we derive

$$\frac{n_-}{n_+} = \exp\left(-\frac{2\kappa\,\Phi_{\mathrm{top}}^{\mathrm{deloc}}}{k_BT}\right) > 1. \tag{12}$$

Typical energies associated with (10) are of about $10^5\,\mathrm{K}$, so that all the values of n_j are usually negligible. However, the contribution of $\Phi_{\mathrm{top}}^{\mathrm{deloc}}$ can shift a minimal positive potential U_-^{eff} to threshold (8) and thus the value of n_- becomes appreciable. Presumably, this is the case in semiconductors such as GaAs. To evaluate this particular event, we adopt the lattice spacing $a = 0.56537\,\mathrm{nm}$ [56] and $\kappa = 3e$, where e is the charge of proton. On utilizing the potential values for the ZnS structure from [34], the expected magnitude of $n_- \approx 10^{-3}$ at $T \approx 1000\,\mathrm{K}$ [41] appears if we invoke $\Phi_{\mathrm{top}}^{\mathrm{deloc}} = -3.757\,\kappa/a$.

To estimate this value in terms of structural ionic parameters, we may assume that there is a close-packed sphalerite structure composed of spherical ions of radii R_{Ga} and R_{As}, but their core regions [29, 57, 58, 59] of
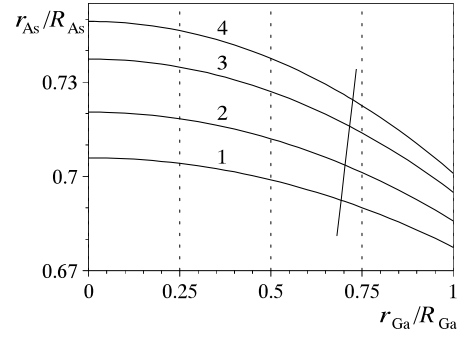

FIG. 1: The ratio $r_{\mathrm{As}}/R_{\mathrm{As}}$ of a core ionic radius to a crystal one for the As^{3-} ion versus that for the Ga^{3+} ion so as to result in the value of $\Phi_{\mathrm{top}}^{\mathrm{deloc}} = -3.757\,\kappa/a$ expected for GaAs. Curves 1, 2, 3, and 4 correspond to $R_{\mathrm{Ga}}/R_{\mathrm{As}} = 0.225$, 0.25, 0.279, and 0.3, respectively. The thin solid line exhibits the case of $r_{\mathrm{As}}/R_{\mathrm{As}} = r_{\mathrm{Ga}}/R_{\mathrm{Ga}}$.

radii r_{Ga} and r_{As}, charged uniformly [19, 20, 25] contribute to $\Phi_{\mathrm{top}}^{\mathrm{deloc}}$. According to (5), it is easy to get [13, 34]
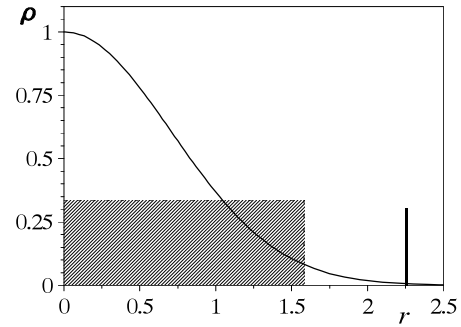

FIG. 2: Gaussian charge distribution $\rho(r) = \exp(-r^2)$ (solid curve) and an equivalent uniform distribution (the hatched area) restricted by $r = r_{\mathrm{ion}}$, whereas the vertical heavy line corresponds to the crystal radius $R_{\mathrm{ion}} = r_{\mathrm{ion}}/0.7$.

TABLE I: Local point-charge-lattice potentials, in units of κ/a, describing Ni_3Sb within the D0$_3$ structure and the corresponding B1 potentials. Sb^{3-} ions are on β sites in the traditional nomenclature [37], but Ni^+ ions occupy α and γ sites specified in units of a in the parentheses.

| Structure	U_β^0 (0,0,0)	U_α^0 $(\frac{1}{4},\frac{1}{4},\frac{1}{4})$	U_γ^0 $(\frac{1}{2},0,0)$
D0$_3$ (BiF$_3$)	11.06098140	−4.07072302	−2.91953536
B1 (NaCl)	3.49512919	0	−3.49512919

FIG. 3: Local point-charge-lattice potentials U_α^0 (line α) and U_γ^0 (line γ) measured in units of κ/a versus the deviation c from the total occupation of α sites. The degenerate case pointed out by the dotted vertical line at $c = 0.248$ corresponds to the $Ni_{71.5}Sb_{28.5}$ composition.

and ions in terms of Gaussian orbitals [61, 62] we have

$$Z_{\text{ion}} = \pi^{3/2}, \qquad \Phi_{\text{top}}^{\text{deloc}} = \frac{\pi^{5/2}}{v}. \qquad (14)$$

The foregoing ionic parameters specified by (13) and (14) and imposed on this charge distribution in Fig. 2 for comparison are in favor of the above assessment.

Note that here we discuss the tendency towards arising vacancies in a perfect system, but not their final states [39, 40, 41]. Both the classical problem [35, 63, 64] of the n-type conductivity in ZnO and that of vacancies in nitrides [43, 44, 45] can be comprehended in the same fashion. The trends in complex defects associated with anion vacancies [39, 42, 65] are clarified as well.

Owing to (8), the above mechanism enforces the stability of cation states and so prevents from cation vacancies as a thermal effect. It means that another nature brings about cation vacancies observed in a large concentration in Ni_3Sb [37]. Of course, the experimental existence of such a state implies the possibility of its thermodynamic description with a large number of relevant parameters [38], but the underlying physical motive remains obscure within such an approach. To elucidate the reason promoting the appearance of this unusual state, we resort to the potential effect associated with structural features.

The stoichiometric Ni_3Sb compound has the D0$_3$ structure [36, 37, 38, 66] that is just the BiF$_3$ one [56], with the local point-charge-lattice potentials listed in Table I [13, 34], where the lattice parameter $a \approx 0.59$ nm [37] and the charge κ on the Ni^+ ion are used as basic units. So, the α states of Ni^+ ions are formally much more stable than the γ ones. Notwithstanding, we must propose that there are structural vacancies on the α sites, in accord with experiment. The change in the local potentials can then be written in the form

$$U_j^0 = (1-c)U_j^0(\text{D0}_3) + c\,U_j^0(\text{B1}), \qquad (15)$$

where c describes the effective admixture of the B1-lattice potentials compiled in Table I as well. Keeping in mind that the B1 lattice is free from charges on α sites, there are two α sites per unit cell with the occupation probability $1-c$ on each. All the other sites are occupied completely, with the charge $\kappa(2c-3)$ on a Sb^{3-} ion for neutrality. The changes in U_α^0 and U_γ^0 defined by (15)
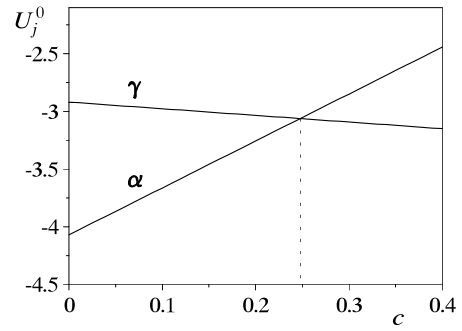
with the potentials from Table I exhibit the principal tendency towards the equalization of the potentials operating on structurally nonequivalent Ni^+ ions, as shown in Fig. 3. It is surprising that the potential degeneracy obtained here takes place just at the chemical composition which is the most prominent in experiments [37].

It is evident that apart from a large number of vacant states, equal potentials on α and γ sites are capable of promoting the extraordinary high Ni diffusivity [67]. Basing on this potential equality, the existence of such a state may presumably be associated with the creation of metallic bonds in the Ni subsystem that is much more effective if all three interpenetrating fcc sublattices composed of Ni^+ ions contribute evenly to their formation. A large number of metallic bonds can in turn depress the effect of local vacancies on the conduction electrons. As a result, the charge transfer determining the actual value of κ is expected to be the same for all Ni^+ ions, in support of the uniform description developed above.

As anticipated, the same trend is inherent in metallic alloys of relative structure [36, 66, 68]. The fact that the Coulomb contribution is to be less pronounced there may be regarded as one more evidence in favor of the potential equalization discussed.

It is worth noting that the present consideration of the effect of relative potentials is nonetheless based on absolute values of local potentials in point-charge lattices [13, 34], so that their combination in form (15) is informative. On the other hand, keeping in mind that the value of U_β^0(D0$_3$) is, in absolute units, close to U_{As}^0, but the number of cations is larger, the effect of $\Phi_{\text{top}}^{\text{deloc}}$ defined like (13) violates relation (8) for anion states and so renders the stoichiometric Ni_3Sb compound unstable, in agreement with experiments [37]. Dynamical effects associated with Ni diffusivity and contributing to $\Phi_{\text{top}}^{\text{deloc}}$ so as to restore (8) at finite c will be discussed elsewhere.

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